

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-173866

(43)Date of publication of application : 08.07.1997

(51)Int.Cl.

B01J 35/04  
B01D 53/86  
B01D 53/94  
B01J 21/04  
B01J 23/42  
F01N 3/02

(21)Application number : 07-343719

(71)Applicant : NIPPON SOKEN INC  
DENSO CORP

(22)Date of filing : 28.12.1995

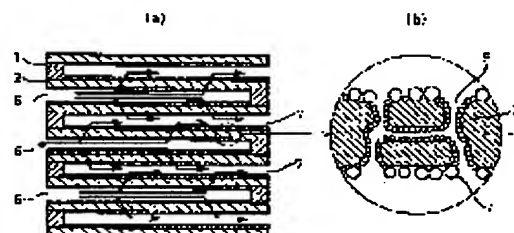
(72)Inventor : NAKANISHI TOMOHIKO  
NAKAYAMA YOSHINORI  
KAGEYAMA TERUTAKA  
KONDO TOSHIHARU

## (54) DIESEL EXHAUST GAS PURIFYING FILTER

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To lower pressure loss while holding a high specific surface area, in a diesel exhaust gas purifying filter passing exhaust gas through the pores of the cell side walls of a honeycomb to allow the same to flow to adjacent cells to collect particulates, by applying active alumina particles mutually different in particle size to the surfaces of cell sidewalls and the inside of cell pores.

**SOLUTION:** Both ends of a monolithic honeycomb are alternately sealed by a sealing material 1 to form a coating layer 4 composed of active alumina particles 3 to the cell side walls 2 of a honeycomb type filter. When diesel exhaust gas containing particulates passes through the cell sidewalls 2, particulates are collected by the surfaces of cell sidewalls and the pores in the cell sidewalls. At this time, a porous coating layer of active alumina A having a particle size larger than the average pore size of the filter is formed on the cell side walls 2 and active alumina B having a small particle size is applied to the inside of cell pores. A wt. ratio of particles A, B is set to a range of  $B/A=2/8-8/2$ .



## LEGAL STATUS

[Date of request for examination]

28.03.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1] Exhaust gas in the cel which passes the pore of the cel side attachment wall of a honeycomb, and adjoins by \*\*\*\*\* (ing) the both ends of cel opening of a ceramic honeycomb structure object by turns A sink, In the porosity ceramic filter which was made to carry out uptake only of the particulate contained in exhaust gas a front face and inside the cel side attachment wall The diesel emission-gas-purification filter characterized by having the porosity coat layer of the activated alumina of the bigger particle size A than the average pore size of a filter in the front face of a cel side attachment wall, and carrying out coating of the activated alumina of the particle size B smaller than the average pore size of a filter to the interior of cel pore.

[Claim 2] The filter according to claim 1 whose ratios of Particle A and Particle B are  $B/A=2/8 - 8/2$  in a weight ratio.

[Claim 3] The filter according to claim 1 or 2 with which the catalyst metal which consists of at least one kind of platinum group metals is supported.

[Claim 4] The filter according to claim 1, 2, or 3 whose average pore size the filter porosity after coating an activated alumina is 5 micrometers or more 35 micrometers or less at 40% or more.

---

[Translation done.]

**\* NOTICES \***

**JPO and NCIPi are not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention removes a particulate at least among the matter contained in the gas discharged by internal combustion engines, such as a diesel power plant, and relates to the filter for particulate uptake used in order to purify exhaust gas.

**[0002]**

**[Description of the Prior Art]** The matter harmful to the body is contained in the particulate discharged by internal combustion engines, such as a diesel power plant, and it has been a technical problem on an environment to remove this. For this reason, in the former, after it carries out uptake of the particulate and it carries out constant-rate uptake with the filter prepared in the exhaust air system of a diesel power plant, the approach of carrying out combustion removal of the particulate by the electric heater, a burner, etc. is performed. Moreover, the combustion temperature of a particulate [ the platinum metal catalyst supported in the filter ] is lowered, and there is also a method of burning continuously the particulate which carried out uptake. In the case of the approach of carrying out combustion removal of the particulate in which the former carried out uptake by the electric heater, a burner, etc., the filter maximum temperature at the time of combustion rises, so that there are many particulate amounts of uptake, a filter may be damaged with the thermal stress concerning a filter, and the particulate amount control of uptake is important, and it has come to control the amount of uptake completely. Since the thermal stress which combustion temperature becomes comparatively low and is applied to a filter becomes small in combustion by the latter catalyst, it excels in thermal resistance.

**[0003]** Generally in the above-mentioned approach, the cordierite which shows low-thermal expansibility is mainly used for particulate uptake as the quality of the material, using the honeycomb structure object of a ceramic in many cases.

**[0004]** Cel opening of one end of the ceramic monolith of honeycomb structure, for example, cel opening by the side of a gas inlet, is \*\*\*\*\*(ed) for the diesel emission-gas-purification filter of this invention every piece, and cel opening by the side of a gas outlet is chisel \*\*\*\*\*(ed) about the cel which opening of an entrance side is not \*\*\*\*\*(ing). Therefore, exhaust gas passes the pore of a cel side attachment wall, and uptake of the particulate which flows with exhaust gas is carried out inside the front face of this cel side attachment wall, and the pore of a cel side attachment wall.

**[0005]**

**[Problem(s) to be Solved by the Invention]** When the porosity ceramic filter of honeycomb structure \*\*\*\*\* the both ends of a monolith honeycomb by turns as mentioned above, gas has an advantage with particulate collection efficiency higher than the filter of other structures for the structure of flowing in the cel which passes the several micrometers - dozens of micrometers pore of a cell wall, and adjoins. In order to support a catalyst in this filter, when coating the interior of a cel side-attachment-wall front face and the pore of a cel side attachment wall with high specific-surface-area ingredients, such as an activated alumina, as that support, there is a problem that pressure loss becomes high compared with the filter which an activated alumina blockades the pore of a cel side attachment wall, and has not coated. Since it will lead to the fall of engine power if the pressure loss of a filter is high, the lower possible one of pressure loss is good. However, in order to make pressure loss low, when the porosity of a filter and a pore diameter are enlarged too much, there is a possibility of reducing particulate collection efficiency.

**[0006]** When coating the ceramic support of honeycomb structure with high specific-surface-area ingredients, such as an activated alumina, some things which specified the particle size of an activated alumina are well-known. Although it has prescribed that activated-alumina particle size is 0.1-100

micrometers by JP,55-1818,B, mixing with amorphous aluminas, such as boehmite, is a premise, it supposes that the bond strength of an activated-alumina coating layer will improve by this, and reference is not made [ that it is only the effectiveness of particle size, and ] clearly. Moreover, in JP,04-80736,B, it is supposed by prescribing that the mean particle diameter of an activated alumina is 20 micrometers or less that it is effective in securing the dispersibility by which the activated-alumina slurry was stabilized, and the bond strength of an activated-alumina coating layer will improve. When the ceramic support of honeycomb structure is coated with an activated alumina, all are aimed at raising bond strength in order to prevent exfoliation of a coating layer.

[0007]

[Means for Solving the Problem] while increasing specific surface area in the porosity ceramic filter of a ceramic honeycomb structure object by forming the porosity coat layer of the activated alumina of the bigger particle size A than the diameter of average porosity of a filter in the front face of a cell side attachment wall, and coating the interior of cell pore with the activated alumina of the particle size B smaller than the average pore size of a filter according to claim 1 -- in addition -- and a pressure loss can be controlled low. According to claim 2, the above-mentioned purpose is well attained by setting a weight ratio to  $B/A = 2/8 - 8/2$  for the ratio of Particle A and Particle B. Like claim 3, a kind of platinum group elements are supported at least as a catalyst metal, and the high catalyst engine performance is realized. According to claim 4, it is prevented that filter porosity makes it low voltage loss after coating when 40% and average pore size make it 5-35 micrometers.

[0008]

[Embodiment of the Invention] In the ceramic filter poured in the cell which passes the pore of the cell wall side of a filter and adjoins exhaust gas when the diesel emission-gas-purification filter of this invention \*\*\*\*\* the both ends of a monolith honeycomb by turns It is related with a filter with catalyst support with the coating layer of high specific-surface-area ingredients, such as an activated alumina, inside all cell side-attachment-wall front faces and the pore of a cell side attachment wall. It is related with the filter produced by the coating approach which controls the increment in the pressure loss of the filter by coating of a high specific-surface-area ingredient, and its approach.

[0009] This invention in this way, by \*\*\*\*\* (ing) the both ends of the porosity monolith honeycomb of honeycomb structure by turns In the porosity honeycomb filter of structure which flows in the cell which gas passes the several micrometers - dozens of micrometers pore of a cell wall, and adjoins In the front face of a cell side attachment wall, it is characterized by carrying out coating of the activated alumina of the particle size inside the pore of a cell side attachment wall with the porosity coat layer smaller than the average pore size of a filter which consists of an activated alumina of a bigger particle size than the average pore size of a filter to homogeneity.

[0010] The base material of the filter used for this invention is cordierite (chemical composition  $2\text{MgO}$ ,  $2\text{Aluminum}_2\text{O}_3$ , and  $5\text{SiO}_2$ ) conventionally known as low-thermal expansion coefficient ceramics, the porosity after coating of an activated alumina is 45% - 60% preferably 40% to 65%, and average pore size uses 5 micrometers - 35 micrometers of porosity and average pore size so that it may be preferably set to 10 micrometers - 30 micrometers.

[0011] On the other hand, a small particle size should coexist with a big particle size substantially more substantially [ the particle size of the high specific-surface-area ingredient with which a filter is coated ] than the average pore size of a filter. If it is going to obtain a predetermined specific surface area with the high specific-surface-area ingredient of single particle size in order to support a platinum group catalyst, when the particle size of a high specific-surface-area ingredient is larger than the average pore size of a filter, if a high specific-surface-area ingredient does not go into the pore inside the cell side attachment wall of a filter, but covers a cell side-attachment-wall front face and the amount of coats increases, the thickness of a coating layer will become thick and a pressure drop buildup will become large. Moreover, when the particle size of a high specific-surface-area ingredient is smaller than the average pore size of a filter, a high specific-surface-area ingredient goes into the pore inside a cell side attachment wall. However, since the thickness of a coating layer will become thick and will bury pore if the amount of coats increases similarly, a pressure drop buildup becomes large. the \*\* which does not bury pore and does not cover a front face completely to coincidence when the diesel emission-gas-purification filter of this invention performs coating for a high specific-surface-area ingredient to both inside a cell side-attachment-wall front face and pore using both a high specific-surface-area ingredient with a big particle size, and a small high specific-surface-area ingredient -- in addition -- and a predetermined specific surface area can be obtained.

[0012] Moreover, the thing that whose a high specific-surface-area ingredient trespasses upon the interior of

the pore of the cel side attachment wall of a filter it is the need is based on the following reasons. Although only the front face of a cel side attachment wall coated the honeycomb mold monolith support of flow through structure with the high specific-surface-area ingredient conventionally, since the particulate contained in exhaust gas stops on the front face of the cel side attachment wall of a filter, and at the interior of the pore of a cel side attachment wall in the case of the honeycomb mold filter of the Wall flow structure where exhaust gas passes through the interior of pore of a cel side attachment wall, a particulate needs to contact inside this high specific-surface-area ingredient and pore at this time in order to receive a catalysis. [0013] the particle (A) of mean particle diameter with a bigger high specific-surface-area ingredient than the average pore size of a filter, and the desirable particle of the particle size of 1.5 times or more of average pore size and the desirable particle (B) of mean particle diameter smaller than the average pore size of a filter -- it is the mixture of the particle of 1/5 or less particle size of average pore size desirably, and compounding ratios are  $B/A=2/8 - 8/2$  in a weight ratio. The probability which a high specific-surface-area ingredient goes that particle size is 1.5 times [ 1/5 to ] the magnitude of average pore size of this into the interior of the pore of a cel side attachment wall, and blockades pore is very large. As for the particle whose mean particle diameter is X, 60% or more of 80% or more of particles usually exists in the particle size of  $X(2/3) - (3/2)X$  within the limits preferably. It is more desirable than this that it is the narrow particle of particle distribution. Moreover, if a compounding ratio is smaller than  $B/A=2/8$ , for a wrap reason, the thickness of a coating layer will become [ a high specific-surface-area ingredient with a big particle size ] thick about a cel side-attachment-wall front face, and a pressure drop buildup will become large. On the contrary, if larger than  $B/A=8/2$ , since a high specific-surface-area ingredient with a small particle size will go into the pore inside a cel side attachment wall and will bury pore, a pressure drop buildup becomes large. [0014] The porosity of the filter after coating a honeycomb mold filter with high specific-surface-area ingredients, such as an activated alumina, by the coating approach of this invention is 40% or more, and if average pore size is 5 micrometers or more 35 micrometers or less, since a pressure loss is low and collection efficiency is high, it is suitable for using it as a diesel particulate filter. while maintaining porosity high like the above, and average pore size by using together a large drop child and a granule child according to this invention -- in addition -- and -- for example, activated-alumina coating of the amount of 20 - 180 g/l is fully possible.

[0015] The diesel emission-gas-purification filter of this invention carries out uptake of the particulate contained in the exhaust gas of a diesel power plant at least, and carries out combustion removal. A filter is coated with high specific-surface-area ingredients, such as an activated alumina, for making a platinum group catalyst metal into the support for carrying out coating. Generally, a platinum group catalyst metal is used as a catalyst which lowers a particulate combustion temperature, and is further used as an oxidation catalyst of a carbon monoxide or a hydrocarbon. The filter of this invention is a filter which has supported the metal catalyst which consists of at least one kind of platinum group metals.

[0016] Next, the diesel emission-gas-purification filter of this invention is concretely explained with drawing 1. Like drawing 1 (a), the porosity ceramic filter of this honeycomb structure forms the coating layer 4 which becomes the cel side attachment wall 2 of a honeycomb mold filter from the activated-alumina particle 3 by \*\*\*\*\* (ing) the both ends of a monolith honeycomb by turns by the \*\*\*\*\* material 1. If the activated alumina of a bigger particle size than the average pore size of a filter and the activated alumina of a small particle size are used like drawing 1 (b), since coating is carried out without the thickness of a wrap coating layer not becoming thick about a cel side-attachment-wall front face, but blockading the interior of the pore 5 of a cel side attachment wall in coincidence, there are few pressure drop buildups of a filter. Moreover, the purification effectiveness of the exhaust gas components (HC, CO, etc.) of a particulate and others by which uptake was carried out to the coating part of an activated alumina by supporting a platinum group catalyst metal inside the cel side-attachment-wall front face and the cel side attachment wall is raised.

[0017] The diesel exhaust gas containing a particulate advances into a cel from the cel entrance side 6, passes a cell wall 2, and leaves it from the cel outlet side 7. At this time, uptake of the particulate is carried out by the pore of a cell wall front face and the interior. Although a platinum group catalyst metal is anew coated after it coats an activated alumina, it is also possible to coat with the solution mixed with the activated alumina.

[0018] The filter coated using the above ingredients can be suitably used as a diesel particulate filter of low voltage loss. Below, the example and example of a comparison are shown.

[0019]

[Example]

[Example 1] A silica, an aluminum hydroxide, and talc are used for the main raw material. It adds. the carbon for adjusting so that it may become a cordierite ( $2\text{MgO}$ ,  $2\text{aluminum}_2\text{O}_3$ , and  $5\text{SiO}_2$ ) presentation, and then making it porosity -- these main raw materials -- receiving -- 20wt(s)% -- Produce a ceramic honeycomb structure object by the well-known extrusion process, and it calcinates by the 1350 degrees C - 1450 degrees C maximum temperature, the programming rate of 5 degrees C - 200 degrees C, and the holding time of 2 - 20 hours. Porosity had the pore property which is 28 micrometers of average pore size 55%, and the porosity cordierite honeycomb structure object with a diameter [ of 140mm ] and a die length of 130mm 0.45mm in cel side-attachment-wall thickness and whose number of cels per 1 square inch are 150 pieces was acquired.

[0020] On the other hand, as a high specific-surface-area ingredient, the addition rate was changed so that the activated alumina (Sumitomo Chemical make) of 5 micrometers of diameters of a centriole and the activated alumina (Sumitomo Chemical make) of 50 micrometers of diameters of a centriole might be set to a total of 670g, alumina sol (product made from Nissan chemistry) 330g was mixed and agitated with 4l. of water, and the activated-alumina slurry was produced.

[0021] The aforementioned porosity cordierite honeycomb structure object is completely dipped in an activated-alumina slurry (wash coat). Then, the slurry which adhered too much in an air cleaner and compression Ayr is removed as completely as possible. Five kinds of honeycombs from which coating is repeated and the amount of coats differs were produced. Furthermore, after that, it dried at 120 degrees C for 2 hours, and calcinated at 800 degrees C. The amount of coats per unit volume was computed from the honeycomb weight difference before and behind a wash coat <amount [g/L] of coats = (after [ a before / a coat / weight-coat ] weight) / honeycomb volume>. Then, after dipping 0.1 mols into the chloroplatinic acid water solution of /L for 30 minutes and making it dry at 120 degrees C for 2 hours, it calcinated at 800 degrees C and platinum was made to support. The amounts of support of platinum were about 2 g/L.

[0022] Cel opening by the side of the gas inlet of the honeycomb structure object which carried out wash coat processing is \*\*\*\*\* (ed) every piece, and it \*\*\*\* [ chisel ] in a gas outlet side about the cel which is not \*\*\*\*\* (ing) by the entrance side. Especially as long as \*\*\*\*\* material is a ceramic ingredient with the thermal resistance of 1000 degrees C or more, such as cordierite, an alumina, and a zirconia, it may not be limited, but the adhesives made from a ceramic are sufficient as it. Thus, the filter with catalyst support was produced. The pressure loss when changing the rate of an activated alumina that particle size differs was investigated at the time of amount of coats 60 g/L. ( Drawing 2 R> 2 )

[0023] [Example 1 of a comparison] The porosity cordierite honeycomb filter used for the example 1 and the same filter were produced by the same approach, and the wash coat of said filter was carried out to the activated-alumina slurry which mixed and agitated 670g (Sumitomo Chemical make) of activated aluminas of 5 micrometers of diameters of a centriole, and alumina sol (product made from Nissan chemistry) 330g with 4l. of water as a high specific-surface-area ingredient. Then, the slurry which adhered too much in an air cleaner and compression Ayr is removed as completely as possible. Coating was repeated and the filter of amount of coats 60 g/L was produced. Furthermore, after that, it dried at 120 degrees C for 2 hours, and calcinated at 800 degrees C. After computing the amount of coats, 0.1 mols are dipped into the chloroplatinic acid water solution of /L for 30 minutes, after making it dry at 120 degrees C for 2 hours, it calcinated at 800 degrees C and platinum was made to support. The amounts of support of platinum were about 2 g/L. Then, cel opening by the side of the gas inlet of the honeycomb structure object which carried out wash coat processing was \*\*\*\*\* (ed) every piece, in the gas outlet side, it \*\*\*\* (ed) [ chisel ] about the cel which is not \*\*\*\*\* (ing) by the entrance side, the filter with catalyst support was produced, and the pressure loss was investigated. ( Drawing 2 )

[0024] [Example 2 of a comparison] The porosity cordierite honeycomb filter used for the example 1 and the same filter were produced by the same approach, and the wash coat of said filter was carried out to the activated-alumina slurry which mixed and agitated 670g (Sumitomo Chemical make) of activated aluminas with a main particle size of about 50 micrometers, and alumina sol (product made from Nissan chemistry) 330g with 4l. of water as a high specific-surface-area ingredient. Then, the slurry which adhered too much in an air cleaner and compression Ayr is removed as completely as possible. Coating was repeated and the filter of amount of coats 60 g/L was produced. Furthermore, after that, it dried at 120 degrees C for 2 hours, and calcinated at 800 degrees C. After computing the amount of coats, 0.1 mols are dipped into the chloroplatinic acid water solution of /L for 30 minutes, after making it dry at 120 degrees C for 2 hours, it calcinated at 800 degrees C and platinum was made to support. The amounts of support of platinum were about 2 g/L. Then, cel opening by the side of the gas inlet of the honeycomb structure object which carried out wash coat processing was \*\*\*\*\* (ed) every piece, in the gas outlet side, it \*\*\*\* (ed) [ chisel ] about the

cel which is not \*\*\*\*\* (ing) by the entrance side, the filter with catalyst support was produced, and the pressure loss was investigated. ( Drawing 2 )

[0025] [Example 2] The porosity cordierite honeycomb filter used for the example 1 and the same filter were produced by the same approach, and the wash coat of said filter was carried out to the activated-alumina slurry which mixed and agitated a total (Sumitomo Chemical make) of the activated alumina of a bigger particle size than the average pore size of a filter, and 670g of activated aluminas of a particle size smaller than the average pore size of a filter, and alumina sol (product made from Nissan chemistry) 330g with 4l. of water as a high specific-surface-area ingredient. It considered as amount of coats 60 g/L, and the filter to which the particle size of an activated alumina was changed was produced. Then, the slurry which adhered too much in an air cleaner and compression Ayr is removed as completely as possible. Furthermore, after that, it dried at 120 degrees C for 2 hours, and calcinated at 800 degrees C. After having dipped into the chloroplatinic acid water solution for 30 minutes after investigating the amount of coats, and making it dry at 120 degrees C for 2 hours, it calcinated at 800 degrees C and platinum was made to support. Then, cel opening by the side of the gas inlet of the honeycomb structure object which carried out wash coat processing was \*\*\*\*\* (ed) every piece, in the gas outlet side, it \*\*\*\*\* (ed) [ chisel ] about the cel which is not \*\*\*\*\* (ing) by the entrance side, the filter with catalyst support was produced, and the relation of a pressure loss was investigated. ( Drawing 3 R> 3)

[0026] [Measurement of the pressure loss of a filter with catalyst support] It is the entrance side of a filter to compression Ayr about all the filters obtained more by examples 1 and 2 and the examples 1 and 2 of a comparison Sink and linear-velocity 1.8 cm/sec The differential pressure of an entrance side and an outlet side was measured. The measurement result of pressure loss is shown in drawing 2 and 3. The diesel emission-gas-purification filter of this invention containing a high specific-surface-area ingredient with a bigger particle size than this result and a small high specific-surface-area ingredient is understood that a pressure loss is lower than the examples 1 and 2 of a comparison which performed coating with the high specific-surface-area ingredient of single particle size in order to obtain a predetermined specific surface area.

---

[Translation done.]

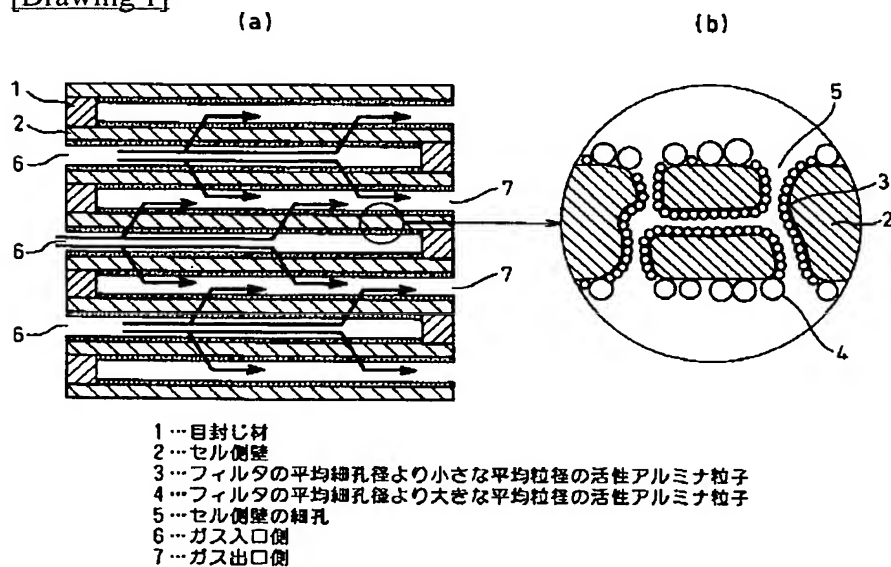
## \* NOTICES \*

JPO and NCIP I are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

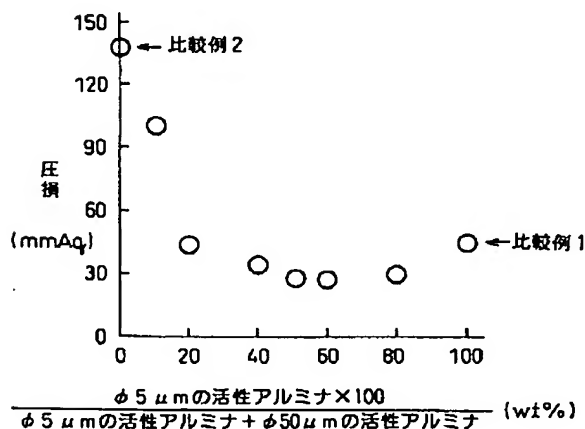
## DRAWINGS

[Drawing 1]



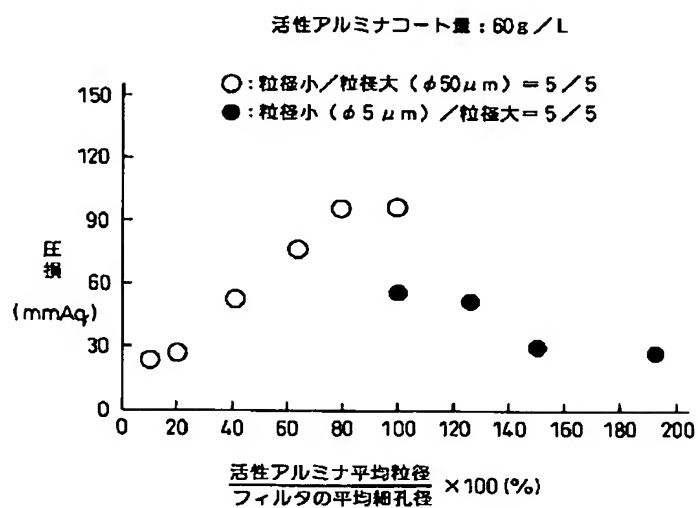
[Drawing 2]

活性アルミナコート量 : 60 g/L



[Drawing 3]





---

[Translation done.]